MULTIPHONON PHOTOEMISSION FROM METALS IN SOLUTION

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The external photoeffect from silver in vacuum, induced by a ruby-laser giant pulse, was investigated for the first time in [1]. However, the observation of multiphonon processes in solids is made complicated by extraneous phenomena such as heating, thermionic emission, and damage to the material. A convenient object for the identification of the multiphonon photoeffect is a photoelectrochemical electrode-solution system, particularly a system consisting of a mercury drop electrode and a photochemically inactive electrolyte. The constant renewal of the surface and the removal of the heat by the solution limits the extraneous effects only to the photocurrents due to changes of the charge density in the electric double layer during pulsed heating and its subsequent relaxation. On a negatively charged surface of mercury, as shown by us earlier [2], the photocurrents due to heating differ in sign from the emission currents. In addition to the foregoing methodological advantage, the theory of photoemission from a metal in a solution, developed in [3], shows the direct connection between the photoemission characteristics and the properties of the metal surface and the structure of the electric double layer, since, unlike a metal-vacuum boundary, the main potential drop occurs across the metal-solution boundary. We present below an equation for the surface photocurrent for n-photon emission from a metal in an electrolyte solution [3]:

$$I_n = A_0 \frac{2\hbar^2}{5k^2\omega_0^{1/2}} \left(\frac{e^2}{\hbar c}\right)^{n-1} \chi_n (n\omega - \omega_0)^{5/2}, \qquad (1)$$

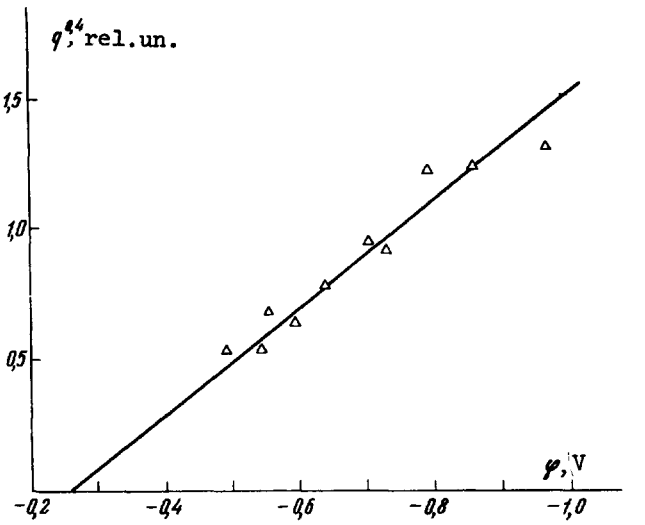
where A_0 is Sommerfeld's constant, ω the frequency of the light, ω_0 the threshold frequency of the effect at zero-charge potential, and χ_n a dimensionless function determined by the properties of the metal and the interface, with $\chi_n \sim L^n$, where L is the light intensity. When the electron is polarized by an amount φ, the work function for the transfer of the metal to the electrolyte changes by an amount $e\varphi$.

In our preceding paper we obtained, by measuring the one-photon photoeffect, a value 3.3 ± 0.15 eV for the work function from mercury in an aqueous solution, at the zero-charge potential of the metal [3]. In the present paper we observed for the first time multiphoton emission from mercury in a solution. To eliminate the reverse current of electrons emitted by the light (from the solution to the electrode), effective electron acceptors, say protons, are introduced into the solution. All the experiments were made in 0.1N and normal perchloric acid. There was practically no reverse current in this case, and the emitted charge is equal to the photocurrent, which is given by (1) multiplied by the illumination duration.

To investigate the multiphoton photoeffect we used ruby and neodymium lasers ($\hbar\omega = 1.785$ and 1.18 eV, respectively). For the ruby laser $2\hbar\omega = 3.57$ eV, i.e., the two-photon emission of the electrons in the solution should start at $\varphi = 0.2$ V relative to the zero-charge point (z.c.p.)*. For the neodymium laser $2\hbar\omega = 2.36$ eV and $3\hbar\omega = 3.54$ eV, i.e., two-photon emis-

sion should start at φ = -1 V and three-photon emission at φ = 0.2 V.

The ruby and neodymium lasers had flash energies of about 1 J and 2 J, respectively, at a flash duration 100 μsec. The laser beam was focused by a long-focus lens (F = 94 mm) on the surface of the mercury drop. A signal proportional to the photocurrent integral picked off a measuring resistor connected in series with the cell was registered by an SI-17 oscilloscope [2].



Current-voltage characteristic of two-photon emission of 0.1N $HClO_4$. φ - potential of saturated calomel electrode.

We investigated the dependence of the photocurrent on the laser emission intensity and on the electrode potential. For a ruby laser $I \sim L^2$, and the dependence of the photocurrent on the potential is a straight line when plotted in coordinates $I^{0.4}$ and φ, in analogy with one-photon processes [2,3] (see the figure). The calculated work function $\hbar\omega_0$ is close to 3.3 eV, the value obtained for one-photon processes. For a neodymium laser, the dependence of the photocurrent on the emission intensity corresponds to $I \sim L^{2.7-3}$ up to φ = -0.5 V (release of hydrogen from the mercury sets in at more negative potentials). For a ruby laser, the charge emitted from the electrode at the z.c.;. is 3×10^{-8} Coul/cm^2 and rises to 2.4×10^{-7} Coul/cm^2 at φ = -0.3 V. For a neodymium laser, the charge emitted at φ = -0.3 V is 8×10^{-9} Coul/cm^2.

From the theory of the photoeffect from metals [4] we have for two- and three-photon processes $I_2 \sim 10^{-21} E^4$ A/cm^2 and $I_3 \sim 10^{-44} E^6$ A/cm^2, where E is the laser emission field intensity in V/cm ($I = q/\Delta t$, where q is the emitted charge and Δt the pulse duration).

Since an estimate of the peak intensities is made complicated by the spike nature of the laser pulses, these intensities were determined accurate to within the order of magnitude. The numerical coefficients obtained at this accuracy coincide with the theory.

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[1] Gy. Farkas, Zs. Naray, and P. Varga, Institute of Physics, Hungarian Academy of Sciences Preprint KFKI 16, 1966.

[2] L. I. Korshunov, Ya. M. Zolotovitskii, and V. A. Benderskii, Zh. Eksp. Teor. Fiz. 54, No. 1 (1968) [Sov. Phys.-JETP 27, No. 1 (1968)].
[3] A. M. Brodskii and Yu. Ya. Gurevich, Elektrokhimiya 3, No. 11 (1967).
[4] F. V. Bunkin and M. V. Fedorov, Zh. Eksp. Teor. Fiz. 48, 1341 (1965) [Sov. Phys.-JETP 21, 896 (1965)].

* All the potentials given above are relative to the z.c.p.

In the article by L. I. Korsunov et al., V. 7, No. 2, p. 42 of the translation, the word "multiphonon" in the title and the first two sentences of the article should be "multiphoton."